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REPORT NO. 5

OF

PROGRESS ON INVESTIGATIONS OF CONFECTIONERY FATS

Period Covered: June 1, 1959-June 1, 1960

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United States Department of Agriculture
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Progress on Investigations of Confectionery Fats

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FOREWORD

Real progress was made in several directions toward providing the confectionery industry with new and valuable products. These include improved cocoa butter-like fats and slab oils. Fundamental information was obtained that will facilitate future research. Thanks are expressed for the encouragement and support of the National Confectioners Association, its Research Advisory Committee, and the member firms offering advice and evaluating the products obtained.

The research described in this report was undertaken on considering the suggestions and recommendations of the Research Advisory Committee of the National Confectioners Association. The research work, particularly that performed by the Fellow of the National Confectioners Association, is believed to conform with the wishes of the Committee.

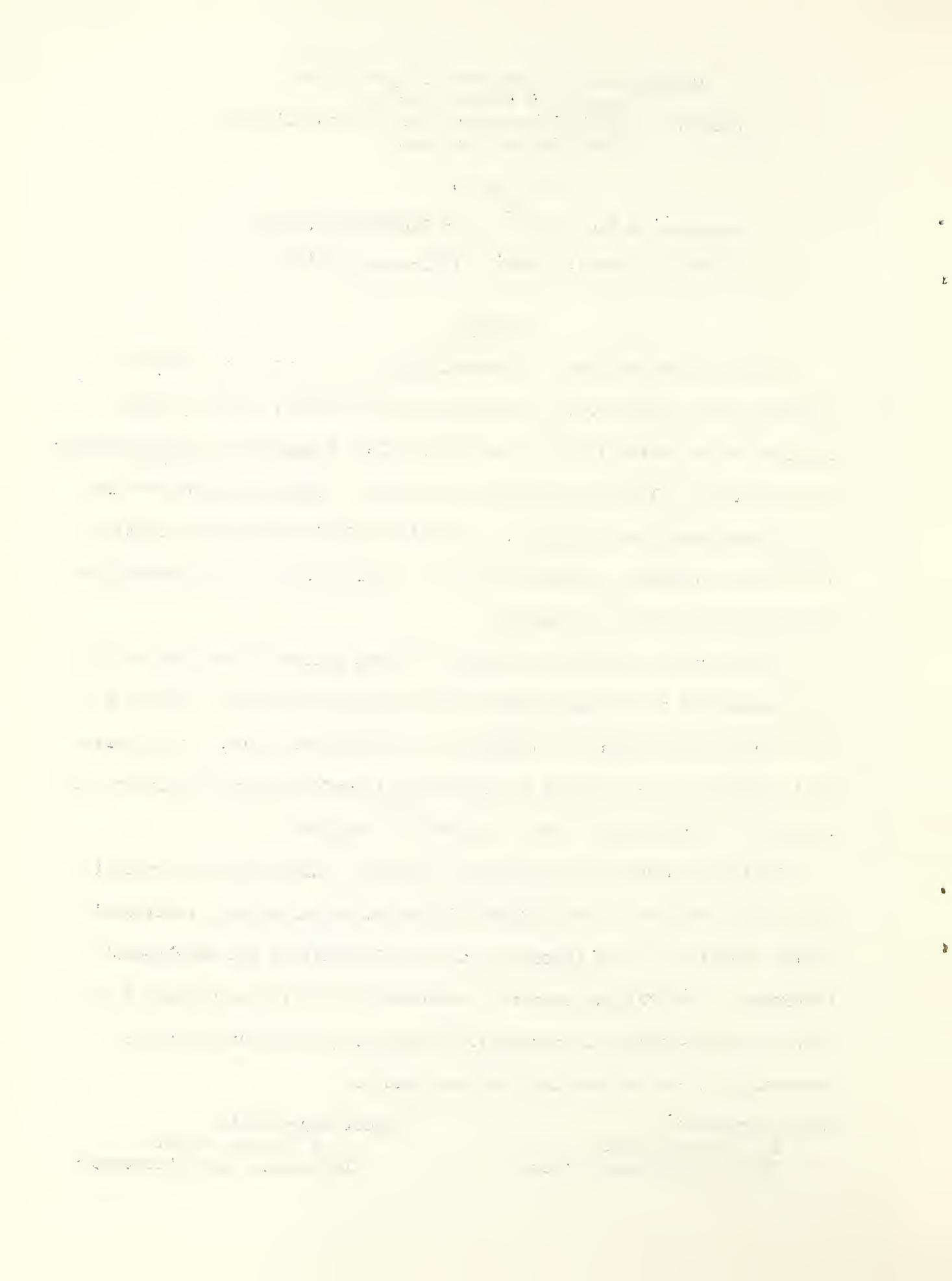
Following previously established practice, this report describes the work of the research team composed of the Fellow and several individuals in the Industrial Crops Laboratory and the Engineering and Development Laboratory. The Fellow personally performed all of the experimental work with the fat 2-palmito-oleostearin, and he carried out various phases of the work on cocoa butter-like fats and slab oils.

Report prepared by:

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Report approved by:

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SUMMARY

Cocoa Butter-Like Fat No. 2, a pilot plant product prepared from completely hydrogenated cottonseed oil and an edible triolein product, was evaluated. Its physical properties were determined in the laboratory and a confectioner made experimental coating compositions with the fat. On the basis of the data obtained, an improved product, Fat No. 3, was prepared. In the preparation of the latter, domestic olive oil was substituted for the triolein product and other processing conditions were changed.

Fats No. 2 and 3 melted mostly over the temperature range associated with cocoa butter. Fat No. 3 was the better product. However, both contained components melting above 100° F. and neither fat would release properly from a mold when solidified in the manner used with cocoa butter. One of the faults, the presence of high melting components, can be corrected in future preparations; and it may be possible to devise molding and solidification techniques which will alleviate the other problem.

To investigate these possibilities a new batch of cocoa butter-like fat is being prepared in the pilot plant. Several pounds of another cocoa butter-like fat have been prepared in the laboratory for investigational purposes.

A highly pure sample of the triglyceride 2-palmito-oleostearin, a component of confectionery fats, was prepared; and its physical properties were determined. The 2-palmito-oleostearin was found to crystallize in three solid forms and to have melting points at 75, 99, and 104.5° F. Unlike 2-oleopalmitostearin, the major component of

cocoa butter, the 2-palmito-oleostearin transforms very rapidly from one solid form to another. A confectionery fat composed mainly of this triglyceride should present no problem in tempering.

Additional experiments were performed on the transmission of moisture through films of confectionery fats. The data obtained indicate the passage of moisture through cocoa butter and other confectionery fats can be varied severalfold by manipulating the manner of solidification and tempering. Experiments in this area are continuing.

An experimental slab oil was prepared and found to be 100 times more resistant to rancidity than cottonseed oil. Preliminary tests have shown the oil to possess a number of other desirable properties.

REPORT

A. Cocoa Butter-Like Fats No. 2 and 3

In the preceding annual report a method was outlined by which it is hoped to produce from domestic fats and oils a reasonably good cocoa butter-like fat. Furthermore, the method is such that it should be suitable, economically and technically, for large-scale use. Briefly, the method consists of mixing completely hydrogenated cottonseed oil and a triolein product at 120° F. in the presence of about 0.2% catalyst to obtain rearrangement of the fat mixture, destroying the catalyst, dissolving the reaction product in a solvent (acetone) and cooling the solution gradually to progressively solidify portions of the reaction product. The cocoa butter-like fraction is collected during this solidification.

Fat No. 1 prepared in the pilot plant by this procedure, contained, as mentioned in the preceding annual report, 20.0% of fats (triglycerides) melting above 98.6° F. To correct this fault, Fat No. 2 was prepared using the same starting materials (completely hydrogenated cottonseed oil and a triolein product) but collecting the fat over a shorter temperature interval. As the discussion below will indicate, Fat No. 2 was an improvement over Fat No. 1, but undesirable characteristics still were present. Fat No. 3 was prepared from completely hydrogenated cottonseed oil and domestic olive oil. In the preparation of Fat No. 3 some changes also were made in the method of processing; namely, the

ratio of solid fat to liquid oil in the starting mixture was changed to 75:25, and the cocoa butter-like fraction was collected over the temperature interval 63 - 34° F. Both Fats No. 2 and 3 were prepared on a pilot plant scale. Some of their characteristics are listed in Table I.

Table I. Data on Cocoa Butter-Like Fats No. 2 and 3.

Property	Fat No. 2	Fat No. 3
Softening point, °F. ^{a/}	107.8	110.3
Melting point, °F. ^{a/}	116.6	121.2
Iodine value	26.3	27.5
Trans isomers, as trielaidin, %	4.8	2.5
Linoleate, %	1.5	2.0

a/ The greater portion of each fat melted well below these temperatures.

Dilatometric Examination. A very short melting range is one of the prized characteristics of cocoa butter. Another is that cocoa butter is hard and brittle at room temperature but melts abruptly below body temperature, 98.6° F. These characteristics are attributed to the fact that approximately 80% of cocoa butter consists of two closely related triglycerides, 2-oleopalmitostearin and 2-oleodistearin. To quantitatively define and compare the melting characteristics of the cocoa butter-like fats and cocoa butter, dilatometric data were obtained. Percentages of liquids which were calculated from these data, are recorded in Table II.

Table II. Liquid Content of Cocoa Butter and Cocoa Butter-Like Fats

Temperature °C.	Temperature °F.	Liquid Content, %					
		Cocoa butter		Fat No. 2		Fat No. 3	
		Tempered	Untempered	Tempered	Untempered	Tempered	Untempered
0	32	0.6	---	2.7	2.1	6.1	
5	41	1.9	1.3	4.0	3.1	9.0	
10	50	4.1	3.8	6.0	3.6	12.6	
15	59	6.8	10.0	8.0	5.1	16.6	
20	68	10.8	19.6	12.7	10.6	28.3	
25	77	16.7	61.4	29.3	22.7	67.0	
30	86	36.1	98.2	48.0	40.3	90.4	
		93.4:100.0					
35	95			83.0	88.0	95.1	
40	104			93.6	96.0	95.7	
45	113			95.5	97.2	97.0	
	114.8:						
50	122			98.8	100.0	100.0	
	126			100.0			

As is evident from the data, the greater portion of each of the two fats melted over the same short temperature interval associated with cocoa butter. Fat No. 3 possessed more desirable melting characteristics than did Fat No. 2. Both contained triglycerides melting well above those found in cocoa butter, which is an undesirable characteristic.

The cocoa butter-like fats further resembled cocoa butter in that when rapidly solidified from a completely liquid state, unstable and low-melting solids tended to form. The percentages of solids for the untempered forms of cocoa butter and Fat No. 3 at various temperatures (Table II) indicate that lack of tempering affects each product in about the same manner.

While the proportions of low-melting solids in quick-chilled samples of cocoa butter-like fats and cocoa butter may be similar, the products behave in a very different manner on tempering. Whereas quick-chilled cocoa butter requires about two weeks of storage at room temperature to convert it into the tempered form, the cocoa butter-like fats could be converted in about two hours. This ease of tempering may be responsible, at least in part, for the failure of the cocoa butter-like fats to contract properly when evaluated in coating formulations.

Contraction on Solidification. The testing of the cocoa butter-like fats in coating compositions, as described below, indicated that a major fault was poor mold release. In these tests, carried out by confectioners, the compositions were handled like chocolate. Measurements made subsequently in our laboratory showed that molding Fat No. 3 under conditions employed in the manufacture of chocolate results in a linear contraction equal to about one-third that for cocoa butter.

Despite these observations, other measurements have shown that the total contraction on solidification is about equal for the cocoa butter-like fats and cocoa butter. On solidification to the well-tempered form, Cocoa Butter-Like Fat No. 2 contracted 8.6% based on the final volume. The contraction for cocoa butter under similar conditions was 9.5%, and for milk chocolate of the coating type about 3%. By way of orientation, under the usual plant conditions, the contractions of cocoa butter and milk chocolate on solidification probably are less than 6% and 2%, respectively. Apparently, in molding chocolate-type formulations containing cocoa butter-like fats, the contraction does not occur at the

proper time. Cooling curves obtained with the several products tend to substantiate this probability. Tests also have shown that cocoa butter can be solidified under conditions which will produce so little contraction that release from the mold becomes difficult. Possibly a special melting, tempering, and molding procedure can be developed for the cocoa butter-like fats which will serve for those applications where mold release is important.

Compatibility with Cocoa Butter. When two different types of fat having about the same melting point and softening range are mixed, each depresses the melting point of the other and the softening range of the mixture is longer than that of the individual fats. Obviously, a good cocoa butter-like fat when mixed with cocoa butter should exhibit these adverse effects to only a limited degree. According to laboratory tests, as more and more of either Fat No. 2 or Fat No. 3 was added to cocoa butter, the melting point of the mixture decreased until a maximum depression of about two Fahrenheit degrees was reached with mixtures containing about 20% of cocoa butter-like fat. Beyond 20% the melting point of the mixture gradually increased to that of the cocoa butter-like fat. Other tests showed that between about 60° and 86° F. a 1:1 mixture of cocoa butter-like fat and cocoa butter contained more liquid oil than did either product alone. The observed incompatibility is not believed to be serious. Some confectionery fats currently on the market have been found to be much more incompatible with cocoa butter; melting point depressions up to about nine Fahrenheit degrees have been observed.

Performance in Coating Compositions. A portion of Cocoa Butter-Like Fat No. 2 was sent to a manufacturer of chocolate who used it to prepare a chocolate-type coating composition. When cooled in preparation for molding, the coating thickened at 120° F. and clung to the walls of the metal container. When solidified, the coating did not contract and release from the mold. However, it was said that the mouthing qualities of the coating were good.

A confectioner tested this same coating and found that to mold properly it had to be heated to 120-125° F. The coating was said to crystallize and solidify more slowly than did a regular coating, but it was not stated if this was due to the higher molding temperature and the need for more heat. The confectioner also stated that the coating was quite waxy and that the mild flavor was delayed in coming through.

Fat No. 3, which was prepared with the objective of overcoming or at least minimizing the undesirable characteristics of Fat No. 2, has been given a preliminary evaluation by the same manufacturer of chocolate who evaluated Fat No. 2. His comments were in part as follows:

".....The presence of fractions melting above 100° F. still presents a problem in handling coatings made from this fat. These fractions apparently separate out as the coating is cooled, and cause a sharp increase in viscosity, interfering with molding or enrobing procedures.

"Our preliminary attempts at a coating made from this fat in accordance with Dr. Feuge's suggestions, still show a failure to contract properly on casting, even in the presence of cocoa butter from the liquor used as flavoring. The seed crystals coming out above 100° F. do not seem to induce complete crystallization of the natural cocoa butter, and the viscosity increase makes normal tempering very difficult.

"We are continuing our experiments in the hope of learning a better way to temper this fat, so that we can make a proper evaluation of it."

Conclusions. Fats No. 2 and 3 apparently proved to be unsatisfactory because they possessed two undesirable characteristics; namely, a fraction of their components melted above 100° F., and the fats when used in coating compositions did not shrink sufficiently after solidification in the molds.

The high-melting fractions can probably be removed in future preparations of fats by including an additional processing step. The problem of insufficient shrinkage on solidification may be overcome or alleviated by the development of special handling techniques or the judicious use of fat mixtures.

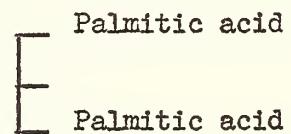
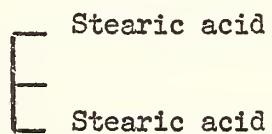
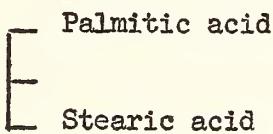
After reviewing the work on cocoa butter-like fats, several members of the Research Advisory Committee of the National Confections Association recommended that research on fats prepared by the method described above should be continued. Apparently, it was their intent that further evaluation be carried out in preference to the investigation of new methods of preparation. Examples were cited in which difficulties encountered at first with some fat products were later overcome.

B. Cocoa Butter-Like Fats No. 4 and 5

The preparation of Fat No. 4 was undertaken to better establish the relationships between the composition of a confectionery fat and its performance characteristics. Originally, it was intended to prepare in the laboratory a fat whose components (triglycerides) were identical with the major components of cocoa butter but which would not contain the minor components of cocoa butter. The two starting materials used

in the preparation were oleic acid and mixed diglycerides of palmitic and stearic acids. Both materials were obtained from commercial producers of fatty products and were of edible grade. Before being used, the diglycerides were treated to remove any free glycerol and the treated mixture was tested to determine several chemical and physical properties. The oleic acid was converted into oleoyl chloride and this was allowed to react with the diglycerides in the presence of an organic base. Approximately eight pounds of Fat No. 4 were prepared.

Unfortunately, Fat No. 4 did not have the expected properties. Even though the examination of the fat has not yet been completed, it appears that unexpected properties were obtained because a portion of the mixed diglycerides of palmitic and stearic acids used in the preparation did not have the presumed spatial arrangement. The general belief has been that diglycerides made in the manner in which these were made would be the 1,3-diglycerides, which may be represented as follows:



where the "E" represents the glycerol portion; and the palmitic and stearic acids are attached to the two outer positions of glycerol as shown. To make the major triglycerides of cocoa butter, the oleic acid would merely have to be added to the vacant middle position. There is now evidence that the mixture contained some 1,2-diglycerides, which may be represented as:

<input type="checkbox"/> Palmitic acid	<input type="checkbox"/> Stearic acid	<input type="checkbox"/> - Palmitic acid
<input type="checkbox"/> Stearic acid	<input type="checkbox"/> Stearic acid	<input type="checkbox"/> - Palmitic acid

After the completion of additional tests, Fat No. 4 may be submitted for evaluation in coating compositions. The greater proportion of its components may yet prove to be identical with those of cocoa butter, and the two products may be quite compatible.

Preparation in the pilot plant of a batch of cocoa butter-like fat similar to Fat No. 3 has been started. This new product (Fat No. 5) will be subjected to an additional filtration step to remove all components melting above 100° F. Approximately 40 pounds of finished product are to be prepared for testing in coating formulations and for use in experiments relating to shrinkage during solidification.

C. Properties of Components of Confectionery Fats

An examination of the melting characteristics and expansivities of a highly purified sample of 2-palmito-oleostearin has been completed. 2-palmito-oleostearin is an isomer (closely related compound) of 2-oleopalmitostearin the major component of cocoa butter, and occurs in cocoa butter-like fats made by interesterification and fractionation.

Samples of the 2-palmito-oleostearin were subjected to various temperature treatments and degrees of tempering, and melting points were determined. So far only the following melting points have been found:

<u>Form</u>	<u>Melting point, °F.</u>
I	104.5
II	99
III	75

The compound probably occurs in one or two additional crystal forms which undergo polymorphic transformations without melting. The two lower melting forms are very unstable. Form III converts to Form II after a few seconds at 72° F. Form II converts to Form I within about 5 minutes at 78° F. Form III can be converted to Form I by holding the former for a reasonable length of time at 50° F.

The 2-palmito-oleostearin differs from the 2-oleopalmitostearin in that the latter has four melting points, namely, 64.8°, 76.1°, 91.4°, and 99.3° F.

There is another difference between the two compounds. Whereas the second highest melting form of 2-oleopalmitostearin requires days of tempering just below its melting point in order to be converted into the highest melting form, the second highest melting form of 2-palmito-oleostearin transforms into the highest melting form in a few minutes. In other words, a confectionery fat composed almost entirely of 2-palmito-oleostearin should present relatively few tempering problems.

From dilatometric data on 2-palmito-oleostearin it was calculated that the melting dilation of Form I at its melting point is 11.7%, which is slightly lower than the 12.4% determined previously for 2-oleopalmitostearin. The expansivity of Form I of 2-palmito-oleostearin was found to be 0.022% per degree Fahrenheit, while the expansivity of the liquid state was found to be 0.042% per degree Fahrenheit. The values for 2-oleopalmitostearin were previously found to be 0.015 and 0.043, respectively.

Experimental work also was performed in another area of research, the melting behavior of known mixtures of fat compounds. However, progress in this area has been slow because difficulties in devising suitable techniques have been encountered. So far the work has been confined to establishing the melting behavior of mixtures of tripalmitin and tristearin. Eventually it is hoped to obtain data on the formation of solid solutions and eutectics in cocoa butter and other confectionery fats.

The information which is being obtained in investigating the physical properties of the components of confectionery fats and of mixtures of these components should be useful in selecting and handling confectionery fats in general, including cocoa butter.

D. Moisture Transmission through Fats

In Report No. 3, the results of an investigation of moisture transmission through confectionery fats was summarized. More detailed and technical descriptions of this work have been published as articles under the titles "Permeability of Some Fat Products to Moisture" and "Moisture Transmission through Fats." Copies can be obtained from the Southern Utilization Research and Development Division. Insofar as is known, these articles are the only ones which have been published on this subject.

At the suggestion of members of the Research Advisory Committee of the National Confectioners Association, additional research work on moisture transmission through fats was performed during the past year.

It was found that the manner in which the films of fat were formed had a large effect on permeability to water vapor. Supposedly slight variations in the melting and solidification procedures produced severalfold variations in the permeability of the films of fat. Apparently crystal size, orientation of the individual crystals, or some related factors have a marked influence. When cocoa butter was heated to just below 96° F., quickly solidified in film form, and stored at room temperature for several days before testing, it was only 1/6 to 1/16 as permeable as films prepared in a similar manner except that the initial melting of the fat was carried out at about 90° F. The permeability of films made from almost completely melted fat increased as the proportion of liquid component at the test temperature increased, which is in accord with the results reported previously. However, the rate at which the permeability increased as the proportion of liquid component increased was less. Also, it was found that cocoa butter from which the normally liquid component had been removed was more permeable to moisture than was whole cocoa butter, when tested under identical conditions. While several possible explanations for the observed behaviors might be offered, there is no proof that they would be correct. Conclusions cannot be drawn at this time. Additional tests are underway. The possibility exists that methods of manipulation can be devised which will be particularly suited for applications requiring a low permeability.

E. Slab Oils

Prior to period covered by this report several samples of a potential slab oil were sent to a number of confectioners. This oil was composed of a mixture of dibutyrostearins and dibutyropalmitins, which are true fats whose building blocks (glycerol and butyric, palmitic, and stearic acids) occur in milk fats. A small amount of food-grade antioxidant was added to the samples before they were sent to the confectioners. The samples were liquid at room temperature and resembled ordinary vegetable oils, except that they were far more resistant to oxidation and rancidity than are vegetable oils.

During the past year evaluations of the oil were received from two confectioners. One made the following comments:

"We have completed the test of the sample Slab Oil which you sent to us on March 13 this year. In testing this, we put some sterile cotton in two bottles, one saturated with mineral oil and one with your sample slab oil. We also made a sample batch of Starlight Kisses with mineral oil and one with your sample oil, and packed each sample in a sealed glass container. I might add that the sample oil was light yellow in color whereas the mineral oil was clear; however, no difference could be detected in the candy.

"The samples were checked periodically each month, and no changes were detected until August 4. At this time the sample oil which was in the bottle with cotton gave off a strong odor, although the odor was not particularly objectionable. The cotton saturated with mineral oil still did not have any odor. However, we were not able to detect any difference in odor or color of the candy made with the two oils. We would conclude from this that the oil would be safe to use.

"We will continue to hold the samples for another few months to see if any other changes occur, and we would like very much to have the results from other manufacturers on this same test.

"These samples were held at room temperature the entire length of the experiments."

The other confectioner made these comments:

"From our check on the slab oil consisting of dibutyropalmitins and dibutyrostearins, we found that it was very satisfactory to use from an experimental basis and do not know of any difficulty that would be encountered when running production batches. It would probably take about five gallons of the slab oil to check some long range effects. Personally, this seems to be about the best that I have seen as a substitute for mineral oil."

Because of the favorable comments which were received, an additional quantity, about five gallons, of the oil was prepared. The method of preparation consisted of heating a mixture of butyric anhydride and purified monoglycerides of palmitic and stearic acids and then removing from the reaction product the unreacted butyric anhydride and the butyric acid which formed as a byproduct. This method, which may not be practical on a large scale, was adopted because it represented the simplest way of obtaining a sizable amount of good product in our laboratory.

The potential slab oil can be prepared almost as easily by another procedure, which is suitable for large-scale use. A small pilot batch has been prepared by this alternate procedure. Completely hydrogenated cottonseed oil and tributyrin (both obtained from commercial suppliers) were mixed and heated for 3/4 hour at about 125° F. A very small amount of sodium ethylate was used as catalyst. The reaction product was purified by removing the catalyst, distilling off the uncombined or excess tributyrin, and then refining the reaction product by the customary procedures used for fats and oils. The finished product possessed very little color and had a bland flavor and odor, indicating that large-scale production from commercially available starting materials is feasible.

A number of tests have been and are being made with the five-gallon batch of experimental slab oil. Some of the data obtained so far are recorded in Table III.

Table III. Experimental Slab Oil

Property	Value
Viscosity, centistokes	
68° F.	41.5
77° F.	33.5
104° F.	18.8
176° F.	6.4
Smoke Point, °F.	311
Flash Point, °F.	459
Fire Point, °F.	525
Cloud Point, °F.	60.0
Pour Point, °F.	50.0
Melting Point, °F.	61.0

At 104° F. the experimental slab oil is about three-fourths as viscous as are coconut and soybean oils and about as viscous as a medium-weight, U.S.P. mineral oil. At 176° F. the viscosity of the experimental oil is about equal to that of coconut and soybean oils.

The smoke, flash, and fire points for the experimental slab oil are somewhat below those of the common vegetable oils but well above those for ordinary, white mineral oil.

The experimental slab oil is extremely resistant to the development of rancidity. Stability tests have shown that the oil did not become rancid after 1500 hours at 208° F., during which time a slow stream of air was passed through the hot oil. In fact, after 1500 hours the oil

was colorless and as bland in flavor and odor as at the start of the test. By way of comparison, under these test conditions lard becomes rancid in 3 to 4 hours; cottonseed oil, 16 to 20 hours; and good vegetable oil shortening, about 300 hours.

The experimental slab oil is practically colorless and bland in flavor and odor. However, a number of individuals have claimed that when the oil is left on the fingers for a very short period of time, a butter-like odor develops. Yet, candies coated with another batch of this oil and stored at room temperature for periods of time up to one year did not develop a butter-like flavor. More tests are indicated.

One-gallon samples of the oil were sent to two confectioners, and four-ounce samples were sent to a number of other individuals. Additional samples are available for testing.

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